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SUMMARY OF TECHNICAL PROGRESS - OVERALL

A goal of work this quarter was to reduce the cost associated with hydride ion reagent "A" (HI "A"). Microautoclave tests were previously conducted using HI "A"/dry coal = 1.0. This quarter, microautoclave tests were completed using a low hydride ion "A"/dry coal ratio (0.2). Glenharold Mine lignite and Black Thunder Mine subbituminous coal conversions were poor at the low ratio. The addition of several reagents to the low hydride ion "A" system did not improve coal conversion. Due to reagent cost at levels required to obtain ca. 90 wt % coal conversion, hydride ion source "A" was eliminated from further consideration in the novel concept process. Hydride ion reagent "D" (HI "D") was suggested as an alternative. This alternative, potentially less expensive, hydride ion source was evaluated in microautoclave tests. When substituted for HI "A" in equimolar amount, coal conversions with HI "D" were found to be greater than 90 wt %

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with Black Thunder Mine subbituminous coal at 375 °C. Cost estimates were developed for this reagent. Evaluation of solvent/coal combinations for high coal conversion in the first stage was continued in microautoclave tests. In all instances, Black Thunder Mine coal conversions were high in anthracene oil. Anthracene oil was selected as the solvent for the process. Black Thunder Mine subbituminous coal was selected for the balance of program.

Baseline one-liter autoclave tests were completed using conditions which simulated British Coal's LSE liquefaction process (410 °C, 60 min, H-donating solvent, solvent/dry coal = 2) and the Wilsonville two-stage liquefaction pilot plant preheater conditions (410 °C, 15 min, 2500 psi H₂ (hot), solvent/dry coal = 1.5). Filtration and catalytic upgrading of these baseline-test products were completed. Filtration of all samples was rapid, regardless of test conditions. The results indicate that hydride ion promoted liquefaction products are more reactive to second-stage conversion than the products of either of these baseline tests. A 300 °C flash of one-liter products was successfully executed. This procedure will be used when the first-stage reactor and the large-scale filter are integrated. Design and construction of the large filter for integration with the one-liter autoclave was completed. Design of the 300 mL second-stage, high-pressure, continuous-flow catalytic reactor system was completed and construction is progressing.

An integrated liquefaction system (ILS) balance was constructed with Run 8-LA test results. ILS results compare favorably with the results achieved in the prospective baseline cases, such as Wilsonville Run 255 and the Australian Brown Coal Liquefaction Project, indicating the potential merit of the Novel Concept approach

SUMMARY OF TECHNICAL PROGRESS - BY TASK

Task 3 - Flow Sheet Development

First-Stage Solubilization

Microautoclave Tests

The feasibility of operating with low hydride ion reagent "A" to dry coal ratios was evaluated in microautoclave scale. The economic projections provided by LDP Assoc. at the end of the last quarter indicated that hydride ion/dry coal ratios greater than 0.2 would be disadvantageous. Tests were made with Glenharold Mine lignite and Black Thunder Mine subbituminous coal at 350 °C and 400 °C. In all cases, coal conversions were poor (ca. 50 wt %) at the low hydride ion reagent to coal ratio. Methanol did little to improve coal conversion when it was introduced into the reaction system. Addition of hydride ion reagent "D" resulted in improved coal

conversions (to ca. 70 wt %) at 350 °C. The addition of NaAlO_2 (a water-gas-shift catalyst) to the reaction system improved coal conversion further (to ca. 80 wt %). At 375 °C, coal conversions obtained with Black Thunder Mine coal using Reilly anthracene oil as solvent, and HI "D" (ca. 90 wt %) were equivalent to those obtained with HI "A" under the same conditions.

Tests were made this quarter using Lummus pasting solvent, Reilly Industries anthracene oil (R-AO), and Kawasaki Steel Corp. anthracene oil (K-AO). Under the same reaction conditions, coal conversions were equivalent or higher with the R-AO. The R-OA was selected as the solvent for the balance of the program. Recycle of the oil will be tested in the next quarter.

There is an economic advantage to the process if low-cost, low-rank coal can be used. As was described above, coal conversions greater than 90 wt % can be obtained with Black Thunder Mine subbituminous coal at low severity conditions (60 min, 375 °C). Consequently, Black Thunder Mine coal was chosen to be the feedstock for the balance of the program.

One-Liter Autoclave

Runs 10-LA, 11-LA, 12-LA, and 13-LA were completed this quarter. Test conditions are provided in Table 1. Run 10-LA was the first one-liter autoclave test made with a 300 °C flash of products from the reactor after the 60 min residence time. The flash at 300°C lowered the reactor pressure from ca. 1000 psi to ca. 200 psi. The flashed material was collected, analyzed, and found to contain water, methanol, and hydride ion reagent "A". A leak developed in Run 10-LA resulting in a poor material balance. However, the products were sent to UK for filtration and second-stage testing. Prior to filtration, the products were distilled by UK and found to contain additional quantities of water, methanol, and hydride ion reagent "A".

Run 11-LA was the first one-liter autoclave test to be made with Reilly Industries anthracene oil. Microautoclave tests showed that this solvent gave superior coal conversions, especially with low-rank coal. The products of this test were flashed at 300 °C, the contents of the reactor were sent to UK for filtration and second-stage catalytic upgrading tests (see below).

The baseline second-stage catalytic upgrading test feed is a Wilsonville pilot plant Run 257 deashed resid. In all tests, the hydride ion promoted liquefaction products are more reactive toward second-stage conversion than this Wilsonville resid. However, the Wilsonville material was recycled in the plant, and the hydride ion promoted materials are single-pass products. To

confirm the higher reactivity of the products produced with hydride ion promoted liquefaction (compared to conventional liquefaction products), two tests were made to produce single-pass products using "conventional" liquefaction conditions. The first test (Run 12-LA) simulated the British Coal's LSE liquefaction process (410 °C, 60 min, H-donating solvent (Lummus pasting solvent), solvent/dry coal = 2). The second test (Run 13-LA) simulated the Wilsonville two-stage liquefaction pilot plant preheater conditions (410 °C, 15 min, 2500 psi H₂ (hot), solvent/dry coal = 1.5). Products of both runs were sent to UK for filtration and second-stage catalytic upgrading (see below).

Filtration Studies

Product from Run 10-LA, a one-liter autoclave run in which the autoclave products were flashed at 300°C (to 200 psi), was reheated in a flask fitted with a condenser prior to transfer to a preheated filter. Initial results indicate a fast filtration rate. Light distillate boiling below 100 °C (7 wt %) was recovered, indicating that about 1/3 of the 'flashed' pressure was due to vapor (water and methanol). Careful re-examination of Run 4-LA product (a sample also produced from Black Thunder Mine coal) indicates that the production of significant quantities of materials boiling between 100 and 300 °C in the first stage had occurred.

Products from a one-liter autoclave test (Run 11-LA) in which Reilly Industries anthracene oil was used as carrier solvent were filtered. Although the Reilly anthracene oil has very little, if any, hydrogen donating capacity, its high aromaticity makes it a good physical solvent. At room temperature, there was no sign of precipitation of high molecular weight extract, in contrast to all previous samples. The absence of a precipitate increased the temperature range over which filtration could be performed without precipitation of heavy material. The sample was split; one-half was filtered at 200 °C and the other at 275 °C. Initial data assessment indicates relatively fast filtration for both runs. However, the 275 °C run filtered about twice as fast as the 200 °C run. Both filtration tests indicated conversions >90 wt %, based upon IOM and ash in the filter cakes.

Products from autoclave runs, which were designed to simulate the first stage of the British Coal LSE process in which a donor solvent is used to extract coal with no overpressure of hydrogen (Run 12-LA) and the early stage of an ITSL- or SRC-type process with 2500 psig over-pressure of hydrogen (Run 13-LA), were filtered. Both autoclave tests were executed at 410 °C. This temperature was higher than any test made to date in the Novel Concept program. These tests

simulated the conventional liquefaction processes in which about 2% hydrogen is added to the coal during initial solubilization. Two filtration runs were performed on each sample and the fast filtration rates were comparable to typical hydride ion-promoted liquefaction runs. Products of Run 13-LA filtered about twice as fast as those from Run 12-LA. However the conversion to THF solubles was lower for Run 13-LA than 12-LA (ca. 75 wt % vs. 93 wt %).

All the filtrates from the above runs were concentrated to give "extracts" with softening points above 200 °C for catalytic upgrading tests (see below).

A large-scale (650 mL total volume) filter was designed, manufactured and delivered with associated heaters for installation on the one-liter first-stage autoclave reactor.

Second-Stage Catalytic Upgrading

To test the sensitivity of resid conversion to H_2 partial pressure, a sample of the filtrate used for the parametric study (NCF28 through NCF32) was hydrotreated at 440 °C for 60 min using 10,000 ppm Mo in as-received Molyvan L. H_2S content was maintained at the usual 2 mol %, but the total pressure was reduced to 718 psig, one-half the normal pressure. Preliminary results indicate that resid conversion, H_2 consumption, and C_1 - C_3 gas make are lower at the lower H_2 pressure. Further data analyses are under way to determine the upgrading efficiency.

Hydrotreated filtrate (produced at 65°C) from Run 8c-LA was upgraded at 440 °C, 60 minutes, 10,000 ppmw Mo as Molyvan L. This sample contains 33 wt % 1050 °F⁺ resid. Resid conversion was 54%. This is 17 wt % lower than the conversion obtained with filtrate produced from Runs 8a/b-LA composite (NCF 28 through NCF 32).

Single catalytic upgrading tests of the filtered products from first-stage Runs 11-LA, 12-LA, and 13-LA were completed. Initial results indicate that the conventional coal liquefaction extracts have lower reactivities than the hydride ion extracts. Resid conversions for the materials produced under the "conventional" liquefaction conditions had resid conversions of ca. 35 wt % (Run 12-LA) and ca. 42 wt % (Run 13-LA). Run 11-LA products, produced with HI "A" had a single-pass resid conversion of ca. 65 wt %. These data are being confirmed.

The high pressure continuous flow continuous stirred tank reactor (CSTR) catalytic upgrading system was designed and constructed. Installation of the 300 mL autoclave high pressure hydrogen gas supply system was begun.

Task 5 - Engineering and Economic Study

Development of the Novel Concept Case

Work on the integrated liquefaction system (ILS) balance with Glenharold Mine lignite was completed (Confidential Appendix 2). Key requirements for completing this balance included: estimation of the first-stage, steady-state recycle solvent composition; reassessment of the first-stage gas yields based on revised data from one liter test Run 8-LA; application of the previously developed carbon balancing procedure to estimate first stage gross and net yields; estimation of first stage light distillate (315 °C-) yield; and estimation of second stage yield factors based on the parametric hydrotreating study.

The results of the ILS balance indicate an excellent C_4^+ distillate yield of approximately 63 wt.% on MAF coal at a low light hydrocarbon gas yield of 6 wt.% on MAF coal. These results are considered preliminary because of the assumptions and estimates required to generate the balance. ILS results compare favorably with the results achieved in the prospective baseline cases, such as Wilsonville Run 255 and the Australian Brown Coal Liquefaction Project, indicating the potential merit of the Novel Concept approach (Tables 2 and 3).

Work on estimating the upgrading of the liquefaction system C_4^+ distillate to gasoline was completed. The results indicate a gasoline yield of approximately 3.3 barrels per ton of moisture free coal fed to liquefaction.

Water Gas Shift Catalysts

Potential commercial suppliers of the water-gas shift catalyst, sodium aluminate were contacted regarding the price for large quantities of this material. There is no domestic production of this material. Europe and Mexico are the main suppliers to the U.S. market. Recommendations were made to use a less costly catalyst, if one is required. Suggestions included potassium carbonate and sodium carbonate (soda ash).

Task 6 - Reporting

All reporting is on schedule. Bi-monthly conference calls were held as scheduled with UK/CAER and LDP. Reports documenting the calls were issued. The quarterly technical review meeting was held on January 15, 1997, at UK/CAER in Lexington, KY, to discuss progress and plans for the direction of the project. A meeting record was issued. A paper entitled "Evaluation of Mo Catalyst Precursors for Hydrotreating Coal Derived Liquids" was submitted for presentation at the 213th National meeting of the American Chemical Society in April 1997 (Appendix 1). A draft Topical Report dealing with all of Task 2 was issued for review.

FORECAST AND PLANS

Task 3 work will concentrate on the use of Black Thunder Mine subbituminous coal and anthracene oil as solvent. Alternative hydride ion sources will continue to be evaluated on a microautoclave scale. To promote first-stage coal conversion, a number of low-cost catalysts will be tested in the first-stage reaction. A material balance one-liter autoclave test is planned with Black Thunder Mine coal and hydride ion reagent "D" (and possibly catalyst). This test will be conducted at conditions that provided high coal conversions in the microautoclave tests. Installation and shake-down of the large-scale filter will be completed by mid-February. Construction of the large-scale catalytic upgrading system will be completed and shake-down tests will be executed by February 1997. Second-stage product quality will be examined. The technical evaluation effort will continue next month to determine fuel gas requirements and the quantity of coal to be gasified to close the make-up hydrogen, make-up carbon monoxide, and fuel gas balances. The process flow sheet will be refined as data from alternative hydride ion sources become available.

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TABLE 1

REACTION CONDITIONS FOR ONE-LITER AUTOCLAVE TESTS
RUNS 10-LA, 11-LA, 12-LA, 13-LA

	10-LA	11-LA	12-LA	13-LA
Temperature, °C	350	350	410	410
Residence Time, min.	60	60	60	15
System Pressure, psig (at T)	1027 ^a	2925	1175	3000
Coal ^b	GH	GH	GH	GH
Solvent ^c	Lummus	R-AO	Lummus	W263 EOR, 488°C-V1074
Solvent/dry Coal, g/g	1.5	1.5	2.0	1.5
Hydride ion reagent "A"/dry coal, g/g	1.0	1.0	-	-
Water (added)/HI "A", mole/mole	1.3	1.3	-	-
H ₂ , psig (cold)		-	-	1050

a. poor material balance; hydride ion "A" loss suspected

b. GH lignite = Glenharold Mine lignite

c. Lummus = Lummus pasting solvent 3LCF7

R-AO = Reilly Industries anthracene oil

W263 EOR, 488°C-V1074 = Wilsonville Run 263, end of run, 488°C distillation fraction, recycle steam

TABLE 2

COMPARISON OF NCLC AND BASE CASE FEED COAL PROPERTIES

Process	wt % MAF		
	Australian BCL	Wilsonville PP	Novel Concept
Feed Coal	Yallourn	Martin Lake	Glenharold
Carbon	67.1	73.3	69.7
Hydrogen	4.7	5.1	4.9
Oxygen	27.5	19.0	22.9
Nitrogen	0.5	1.4	1.0
Sulfur	0.2	1.2	1.5
Total	100.0	100.0	100.0
wt % Ash, MF	1.8	12.3	9.5 (SO ₃ -Free Basis)
wt % Moisture, AR	65	30	35

TABLE 3

COMPARISON OF NOVEL CONCEPT AND BASE CASE YIELDS

Process	Yield, wt % MAF		
	Australian BCL	Wilsonville PP	Novel Concept
	50 T/D Pilot Plant	Run 255	Preliminary
H ₂ O	15.0	15.2	0.7
NH ₃ + H ₂ S	1.1	1.8	1.6
CO + CO ₂	13.9	6.9	53.8
Hydrocarbon Gas	10.6	----	----
C ₁ -C ₃	----	7.6	6.0
Oil	51.1	----	----
C ₄ ⁺ Distillate	----	50.1	62.9
Bottoms	13.9	24.0	16.6
Total	105.6	105.6	141.6
Hydrogen Consumed	5.6	5.6	4.2
CO Consumed*	None	None	37.4
Distillate/Oil EP, °C	420	538	488

*H₂ Equivalent = 2.7

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